CHEMICAL REACTION IN LOW AND ZERO GRAVITY
A FEASIBILITY STUDY

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ABSTRACT

This paper presents the results of a theoretical study to determine the effect of low and zero-gravity on chemical reactions, specifically catalytic polymerization of ethylene using transition metal complexes. Fixed bed, slurry reactor, and fluidized bed polymerization processes are compared under earth gravity and low or zero gravity conditions. Fixed bed polymerization under low or zero gravity does not offer any particular advantages or disadvantages compared to normal gravity processing.

Polymerization in slurry reactors does not appear to be advantageous at this time because the introduction of gas in liquid under a zero gravity environment involves wholly new concepts of bubble formation, growth, and motion, and liquid-gas separation. Comparison of two-phase (gas-solid), stirred fluidized bed polymerization under normal and zero gravity conditions indicates that it would be possible to obtain longer contact times between gaseous monomers and solid catalysts, more rapid heat transfer, lower power requirements, and improved catalyst regeneration capability. A theoretical model of the chemical and physical interactions of the gas and solid phases under normal and reduced gravity is described. This model is used to evaluate the potential performance of slurry and fluidized bed reactors. Techniques are proposed to adapt fluidized bed polymerization for zero-gravity operation. An earth-based approximation of a low-gravity fluidized bed reaction is also described. The approach outlined in this paper might serve as a guide for future studies of space polymerization of other materials.

INTRODUCTION

Manufacturing in space is becoming an exciting and important aspect of our overall space effort. It is exciting because new freedoms are provided with the unique combination of low and zero-gravity forces, unlimited space, and high vacuum. We may be able to utilize these factors to make existing earthbound procedures more attractive and to create new processes and materials not now available to man. The significant aspect arises when determining man's role in space. As interesting as scientific research and experimentation is, the real impact will be made in performing productive tasks that will affect the industrial and economic elements of society.

In exploring the behavior of chemical reactions and processes in a low-gravity space environment, several interesting phenomena were noted. The most basic is the general independence of chemical reactions from gravity. This is primarily due to the small mass of the molecules and atoms involved in these reactions. It was also found that the radiation and vacuum available in space can be used to great advantage to initiate and assist chemical reactions. It is our intent to consider utilization of zero gravity because of its truly unique quality.

Gravity does play a role, however, in large-particle chemistry or polymerization. Many of the present polymerization processes use solid particles to catalyze various reactions. This paper examines the possible beneficial aspects of low and zero gravity for two-phase reaction processes involving a solid phase in a fluid medium. Specifically, the continuous production of polyethylene is investigated for solid catalyzed polymerization in which solid particles are conveyed by either liquid or gaseous phases. Polyethylene polymerization is selected for study because it is a widely used process having a minimum of unknown factors.

Post-reaction, low-gravity separation of two and sometimes three phases, and mixing and flow within a proposed reactor are examined and compared with similar processes on earth. The advantages and problems encountered in this type of processing are probably typical of the many commercial solid-fluid processes. Compared to the suspension and emulsion polymerization processes, the fluidized-bed process is the most attractive under zero-gravity conditions because the free-floating particles can be most efficiently utilized.

Solid particles may be suspended in a gas or liquid phase, forming a fluidized bed, a contacting system which has been successfully used in reaction processes such as the catalytic cracking and reforming of gasoline, and the production of iron from its ore. On earth the fluidized particles attain a suspended state when the gravitational (minus the buoyant) forces on the particles are counterbalanced by the drag forces of the continuous gas or liquid stream. In gas-solid systems in particular, the gas rises in two paths, one a smooth path through the solids and the other a series of bubbles. The bubbles are unlike those in a pure liquid and are associated with the vigorous mixing process of the bed, a process which accounts for its excellent heat transfer properties. The bubbles are disadvantageous for reaction in that a good portion of the gas may bypass the bulk of the solid particles. In reduced gravity flow, little excess gas is required to suspend the particles and longer contact times between gaseous reactants and the solid are possible. Some new process problems are anticipated but they are not expected to be particularly troublesome.

OLEFIN POLYMERIZATION UNDER NORMAL GRAVITY

The early catalytic polymerizations with transition metal complexes were brought to a profitable manufacturing stage with the work of K. Ziegler and coworkers (1, 2, 3), who used titanium tetrachloride reduced in situ with a metal alkyl, the cocatalyst. The most renowned of his systems is that composed of $TiCl_4$ and trialkylaluminum in which chloride ions are stripped from the tetrachlorides, and $TiCl_3$ precipitates from the solution. The initial procedure is still in use, and new catalysts having similar mechanistic features have been developed. This is represented schematically in Figure 1. The primary systems considered in this study are those in which a preformed solid catalyst is distributed in a liquid and/or gaseous phase. Because of an induction period for precipitation and catalysis, a long holdup time is required for continuous operation. Chlorobenzene has been effectively added to the hydrocarbon solvent in an effort to reduce the induction period.

Transition Metal Halides

In a number of investigations, Natta, et al. (4-9) developed a feasible mechanism for the stereoregular polymerizations. They found it would be possible to precrystallize $TiCl_3$ and that the use of a precipitation step with its induction period was unnecessary. A dry milling operation may be used (9) to produce a finely divided $TiCl_3$ powder.

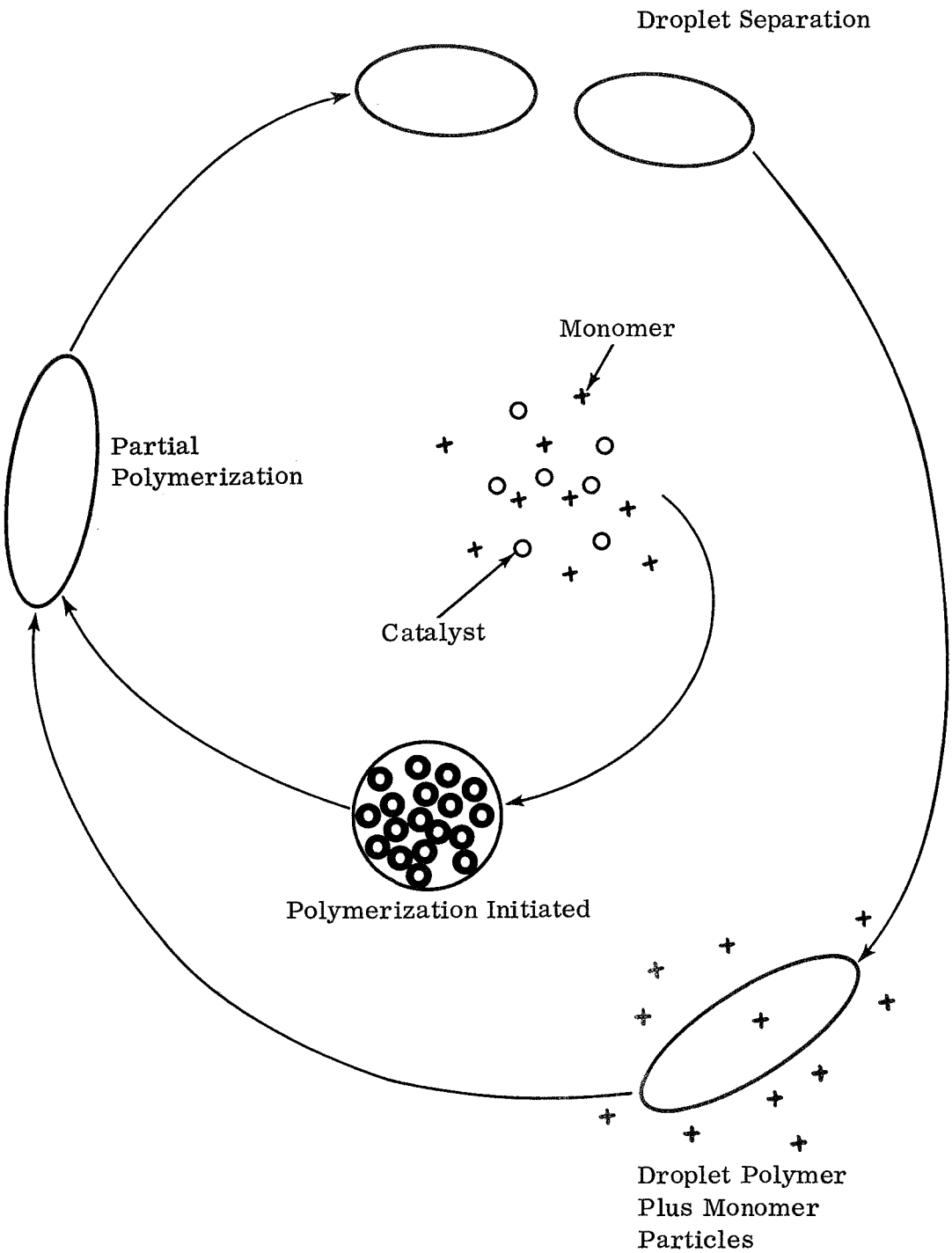


Figure 1. Typical Polymerization Reaction

The product is susceptible to degradation by both oxygen and moisture. In the purification process the catalyst may be deactivated by an alcohol wash. Other transition metal halides were also found to be sufficiently active catalysts (for example, the chlorides of vanadium, chromium, and zirconium). The molecular weight of polymers produced is related to the ratio of reducing agent to catalyst as well as to the total quantity of catalyst. Adding hydrogen gas decreases the molecular weight and adding diluting gas reduces the rate of reaction. Natta (10) and Schindler (11) have proposed the following mechanism for propagation:

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - (CH_2 - CH_2)_n - R} + CH_2 = CH_2 \xrightarrow{k_1}$$

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - (CH_2 - CH_2)_{n+1} - R}$$

The termination may be by a transfer reaction,

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - R} + CH_2 = CH_2 \xrightarrow{k_2} \overset{(+)\ (-)}{X\ CH_2 - CH_2} + CH_2 = CH - R$$

or by hydride formation,

$$\overset{(+)\ (-)}{X\ CH_2 - CH_2 - R} \xrightarrow{k_3} \overset{(+)\ (-)}{X\ H} + CH_2 = CH - R$$

A side reaction which is also likely to occur is

$$\overset{(+)\ (-)}{X\ H} + CH_2 = CH_2 \xrightarrow{k_4} \overset{(+)\ (-)}{X\ CH_2 - CH_3}$$

The propagation rate, assuming steady state in all but the propagation reaction, is given by

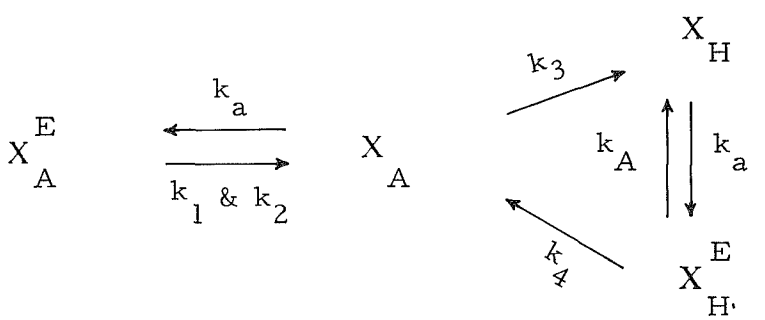
$$R_p = k_1 C_M C_E = (k_4/k_3)\, k_1 C_o C_E^{\,2} \Big/ \left[(k_4/k_3)\, C_E + 1 \right]$$

in which: C_M, C_H are the concentration of sites with metal-alkyl bonds (on which propagation occurs) and with hydrided or terminated bonds, respectively

$C_o = C_M + C_H$ = Total concentration of active sites

C_E = effective concentration of ethylene

Schindler (11) has shown that if the rate of adsorption controls the overall propagation rate a similar form of expression results. In this instance, let X represent catalyst sites as shown below:



Constants and superscripts are defined as follows:

k_a and k_d = adsorption and desorption rate constants for ethylene

superscript E = ethylene

subscripts A, H = active alkyl bond and latent hydride bond, respectively

In this case, $R_p = C_E^{\,2}/(B_o + A_o C_E)$

where $A_o = (k_1 + k_2)/k_a k_1 C_{xo}$, $B_o = k_3(k_1 + k_2)(k_4 + k_d)/k_4 k_a^{\,2} k_1 C_{xo}$

Although this mechanism confirms the often found result that the rate is proportional to either a first or second power of the ethylene concentration, some experimental evidence indicates that the rate becomes second order as C_E increases. This condition may be fit empirically by

$$R_p = kC_E (1 + KC_E)$$

where k and K are empirically derived constants. Rate expressions for ethylene and propylene are given in Appendix 1.

Transition Metal Oxides

Standard Oil (Indiana) Reaction. The preferred catalyst consists of a γ-alumina support impregnated with 8% MoO_3 activated by treatment with hydrogen, and then promoted by a reducing agent such as calcium hydride. The catalyst size varies from 4-6 mesh for fixed bed operation to 20-85 mesh for slurry operation (12). Polymerization temperatures range from 75 to 300°C and pressures from 500 to 1500 psig. The reaction may be carried out in either a solution or a suspension phase, depending on whether or not the polymer formed is soluble in the carrier solvent.

Phillips Petroleum Reaction. The catalyst consists of an SiO_2/Al_2O_3 = 9 support on which 3% chromium oxide is impregnated. Ethylene in solution is usually fed to the catalyst; the solvent is eventually used for extraction. The catalyst size is probably similar to that used in the Standard Oil Processes, except for the gas fluidized bed version with size range 40-100 mesh. Solution polymerization uses temperatures of 130-170°C with a pressure of about 400-600 psig. Suspension and fluidized beds operate at lower temperatures, (90-110°C). See Appendix 2 for additional details on Phillips catalyst and solvent.

OLEFIN POLYMERIZATION PROCESSES

Earthbound Processes

Fixed Bed. A 5-10 wt. % solution of ethylene is fed in the Standard Oil process (13-16) or 2-4% in the Phillips process, the latter at an hourly space velocity of 1.0-6.0 liquid phase (17). In the fixed bed

processes some major problems may occur. Because of the poor heat transfer through the bed, high localized temperatures may result causing increased polymer agglomeration, catalyst degradation, and loss of selectivity. If no heat were removed from the reaction, the total conversion of ethylene would leave the product 1000° hotter than the starting temperature (18). One of the reasons for feeding a low percent of ethylene at fairly high space velocity is to partially overcome this problem. Power losses due to pressure drop across the bed will increase as the extent of polymerization increases, thus increasing pumping costs. Operation at high temperature is required to keep polymer in solution. Also, in cases of severe channeling, some of the solution-containing monomer may bypass a good portion of the catalyst.

Slurry Reactor. The catalyst particles are stirred in an autoclave which may be operated in either a continuous or a batch fashion. The autoclave is baffled in such a manner that the lower portion of the vessel is stirred vigorously while the upper portion remains quiescent. The main problems with slurry operation are the fairly high costs of power consumption. The use of finer particles and higher liquid velocities partially reduce the necessary power requirements. Heat transfer problems are usually brought under control by cooling jackets.

Fluidized Bed. In one version of the Phillips process, a stream of gaseous ethylene is fed through a fluidized bed of particles. The reaction is initiated at 260 psig to coat the catalyst in order to prevent premature agglomeration and then is raised over 80 minutes to the operating level of 450 psig for the remainder of the reaction. An average reaction rate of 13 g/polymer/hr/gm-catalyst has been reported (19). A much finer particle size and the highest ethylene velocities are required in this process. This is represented schematically in Figure 2. Additional information on the process may be found in Appendix 3. Some reactant gas bypasses the catalyst as bubbles but the heat transfer is excellent in this process. Heat removal may be expedited by liquid film boiling as described in Appendix 4.

Low Gravity Processes

Fixed Bed. In order to maintain a fixed bed condition in low or zero gravity, either downflow or an additional screen will be required. No benefits or disadvantages of this type of operation is expected outside of earth's gravitational force.

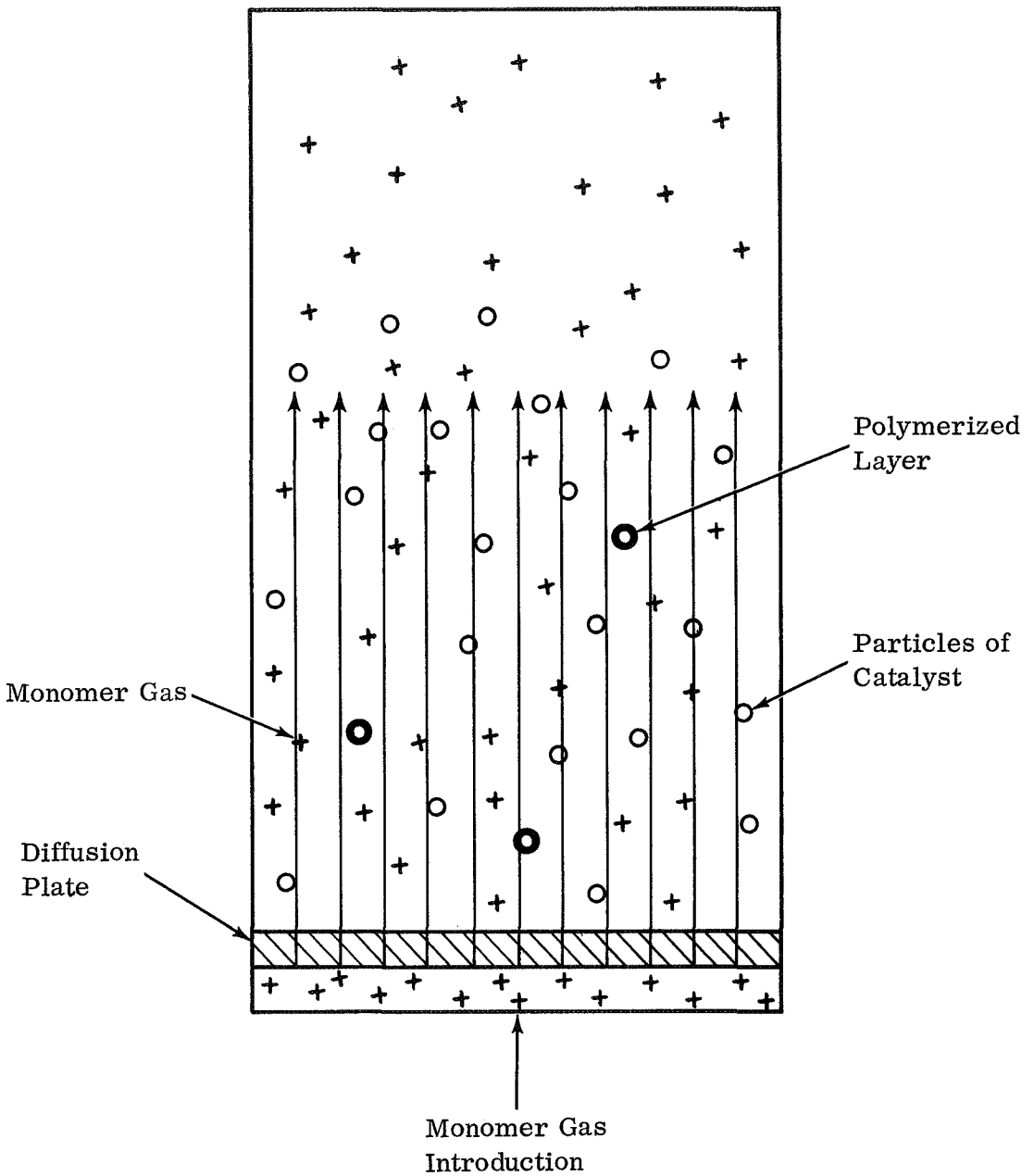


Figure 2. Fluidized Bed Polymerization

Slurry Reactor (Fluid-Solid Conveying). A diagram of the proposed slurry type reactor is presented in Figure 3. At start up, liquid iso-octane is fed to the stirred reactor with the stirrer on. Gaseous ethylene is then fed to the reactor whose design minimizes bubble formation at the stirrer. The slurry passes through a vaporizer where it is stripped of ethylene and through a fractionator where it is stripped of iso-octane solvent. All the vaporization units are designed according to the methods suggested by Otto (20). Their reliability is somewhat of an unknown, particularly those units in the presence of solids. In Figure 3, one such device is depicted as one spherical vessel with an eccentric smaller sphere. The bubbles, it is claimed, travel in the direction of its greatest sphericity. Larger particles than those ordinarily used for slurries may be charged since no gravitational forces need be overcome.

The slurry should pass through the pipelines more readily than under 1g, since a reduced saltation phenomenon would exist at low g, resulting in the need for lower gas velocities to keep particles suspended.

Fluidized Bed (Stirred and Semi-continuous). Most of the processes previously described may be undertaken as fixed, moving, and fluidized beds or as a slurry process. Except for the fluidized bed process, they are all three-phase processes involving solid, liquid, and gas. Under zero gravity it may be advantageous to concentrate on gas-solid systems, rather than gas-solid-liquid systems, since introduction of gas in liquid under zero gravity environment involves wholly new concepts of bubble formation, growth and motion, and liquid-gas separation.

One cannot, of course, create an ordinary fluidized bed in a zero-gravity environment, since in the absence of a gravitational force, even low velocities of the gas would cause the particles to move along with the gas. However, one may still achieve solid circulation in the gas phase by mechanical agitation. In the absence of gravitational forces the power requirements for keeping the particles in suspension would be low, i.e., the intensity of mechanical agitation need not be as severe. Hence, one could visualize a reactor with the reactant gas being dispersed through the vessel and having the stirrer as near the exit as possible. Such a system would offer the basic advantage of a fluidized bed, i.e., improved heat transfer and low temperature gradients in the system with reduced power requirements. Another advantage is that regeneration of the catalyst can be undertaken in situ as compared with the slurry process where solid-liquid separation must be accomplished.

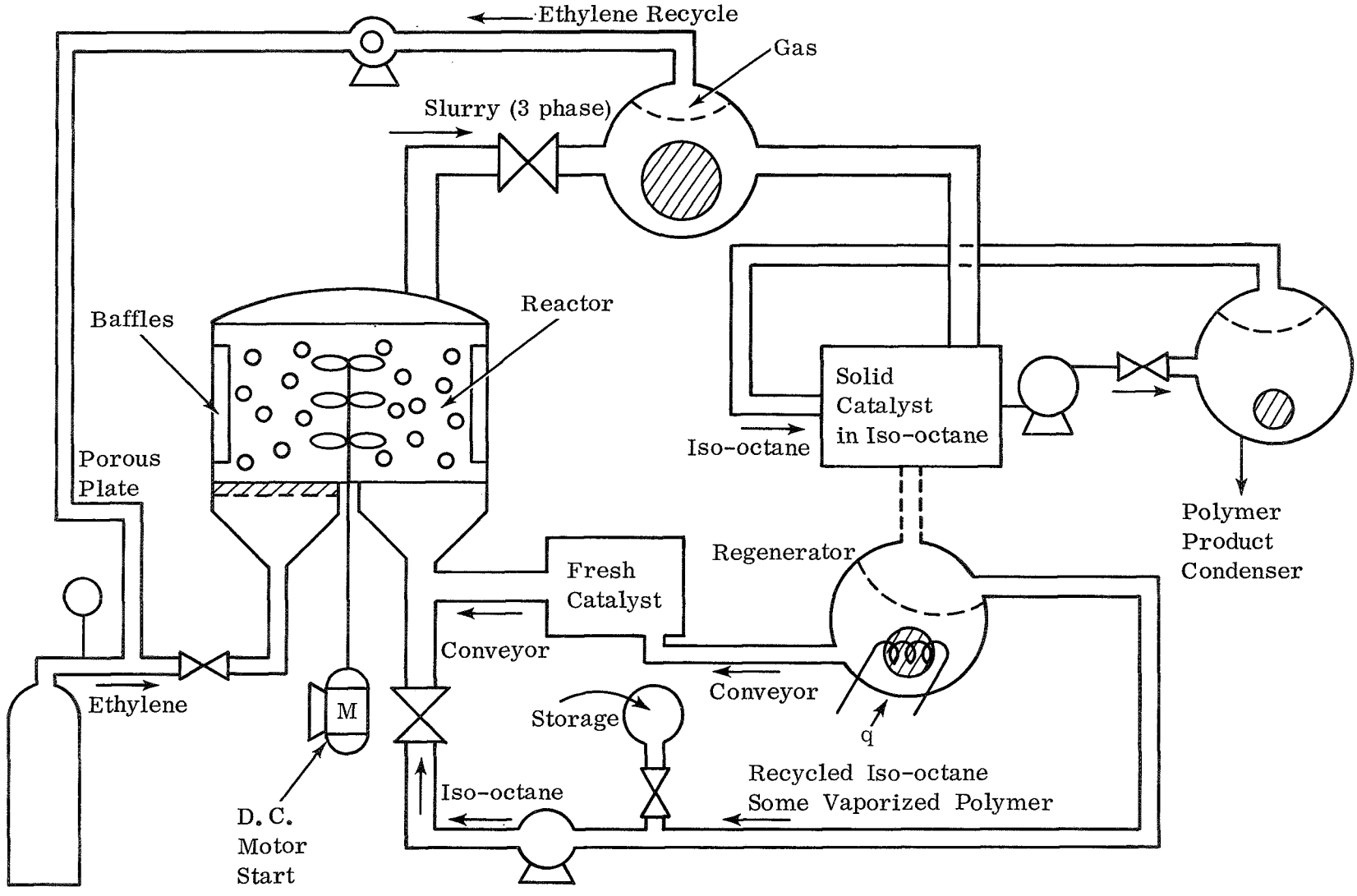


Figure 3. Zero Gravity Slurry Type Reactor

Polymer on the catalyst may be recovered by stripping the catalyst with an inert gas such as nitrogen at a high temperature (700° to 1100°F or higher); the effluent stripping gas would be cooled to condense the polymer removed therein.

Regeneration may be carried out periodically using oxygen at 540°C. An alternative is to dissolve the catalyst in solvent as described in Appendix 2. Figure 4 is a flowsheet of the stirred fluidized bed reactor-regenerator process. Valve 1 is closed for ethylene feed which reacts in vessel on a semi-batch basis. Valve 2 is opened at the conclusion of the reaction and the catalyst is stripped with nitrogen. Periodically, oxygen is fed to regenerate the catalyst's activity. This is followed by a nitrogen purge.

MODEL FOR LOW-GRAVITY REACTIONS

A mathematical model of the proposed zero-gravity reactions is presented in Appendix 5 for your further consideration.

GRAVITY SIMULATION TECHNIQUES

In the processes described previously, some questions arise as to the flow and transport of gaseous and solid phases in low gravity. An earth-based experimental approximation of the low-gravity fluidized bed could be made using magnetic iron oxide for the catalyst core. The techniques of Papell (21) which worked well for colloidal suspensions are described in detail in Appendix 4.

Simple transport process studies including bubble phenomena and particle motions may also be investigated in drop tower or projectile simulations. Such two-phase studies should also provide much needed data for the solution of heat transfer and solids transport problems in zero-gravity conditions. The complete mixing assumption is a limiting condition which is expected to hold in both zero-gravity processes. Simulation of the mixing process, however, would make it possible to apply more sophisticated mathematical models, pinpoint problem areas, and facilitate flight experiment design.

CONCLUSIONS

Polymerization in a zero-gravity environment appears to have certain distinct advantages over earthbound polymerization. Power inputs would be lower. In addition, reactant and catalyst would be allowed to

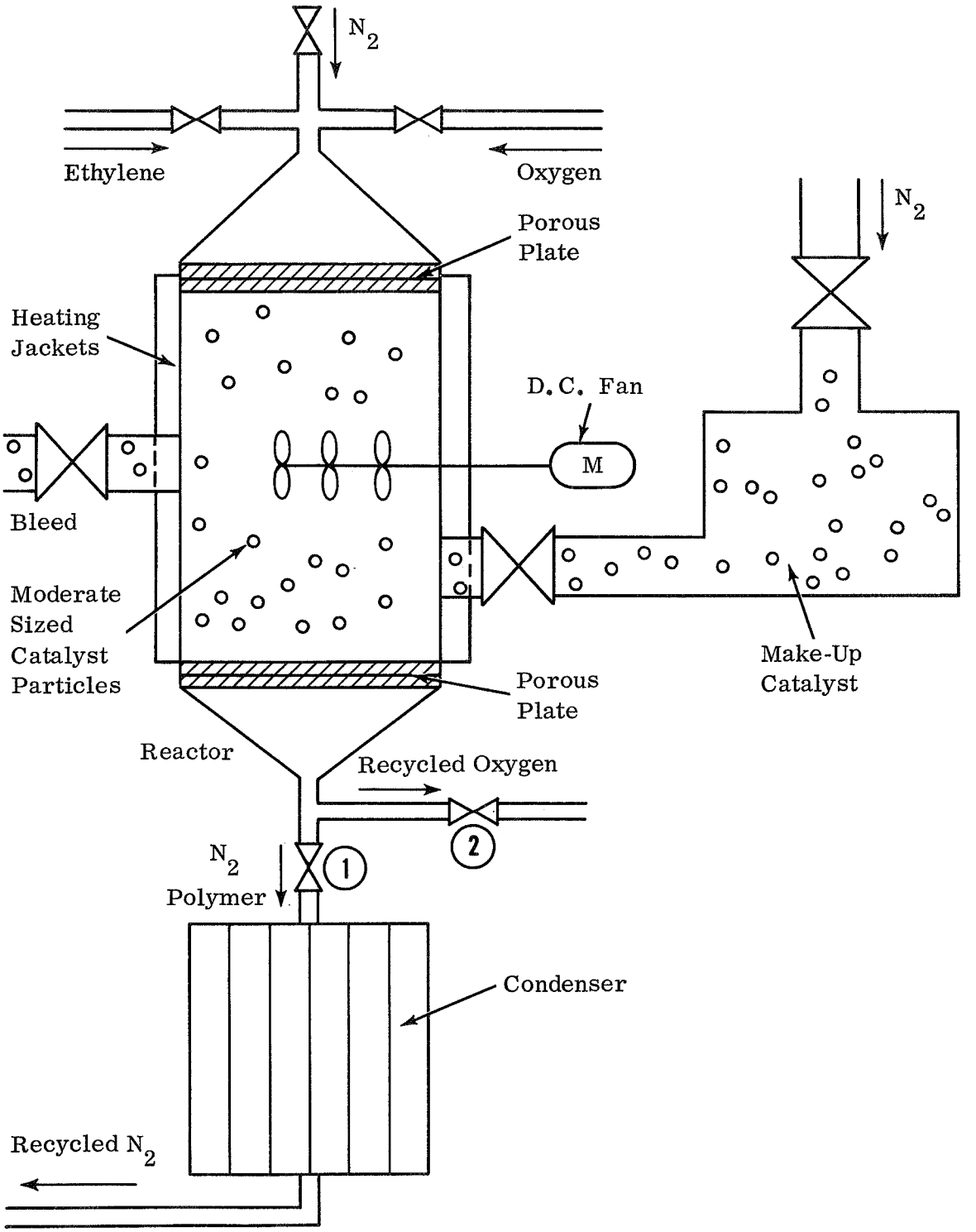


Figure 4. Stirred Fluidized Bed

mix intimately and still give a good heat transfer rate. Fluidized bed polymerization under zero-gravity conditions offers the most advantages over other polymerization processes.

Ethylene polymerization in space -- the particular example used in this analysis -- would not be economically competitive with earthbound polyethylene production because of the relatively low cost of the end product (about ten cents per pound). Studies to determine the feasibility of space polymerizing more complex molecular products having high dollar values per pound should be pursued. The principles discussed in this paper might also be applicable to biochemical products, especially space manufacture of protein food supplements.

It should be kept in mind that the concepts presented in this paper are not intended to answer all the questions relating to space manufacture of chemical raw materials but rather should serve as a guide to generate new approaches for future studies.

The authors wish to thank Dr. Edward Ziegler of the Polytechnic Institute of Brooklyn without whose assistance this paper could not have been written.

APPENDIX 1. RATE EXPRESSIONS

Ethylene.

Activation energies: $TiCl_4/Al(i\text{-}Bu)_3$, $\Delta E = 10.4$ k cal/g-mole

$Ti(OBu)_4/Al\ Et_3$, $\Delta E = 13$ k cal/g-mole

Propylene. From Natta (22),

$$R_p \text{ (gms } C_3 \text{ reacted/hr)} = k_o G_{TiCl_3} \text{ (grams) } P_{C_3H_6} \text{ (atm)} e^{-\Delta E/RT}$$

$$k_o = 2 - 3.4 \times 10^7 \text{ (hr-atm)}^{-1}$$

$$\Delta E = 10 \text{ k cal/g-mole}$$

APPENDIX 2. DETAILS ON PHILLIP'S CATALYST AND SOLVENTS

Solvent:

Inert liquid under reaction conditions which does not deactivate the catalyst should be used. Saturated aliphatic compounds are more suitable than aromatic compounds since they do not undergo alkylation reactions. Cyclohexane has a high boiling point and adequate solvent power for polyethylene. The solvent is used in slurry process or for removal of polymer from the catalyst.

Catalyst Preparation:

Commercially available silica-alumina is suitable as a support. The productivity of the catalyst does not increase with chromium content greater than three-to-one. The chromium is deposited on the support by impregnation with aqueous solutions of any chromium compound that can decompose to chromium oxide when exposed to dry air at 540°C. This activation treatment is required to dehydrate the catalyst to a sufficiently low level and to oxidize at least two-thirds of the chromium to the hexavalent state. The silica-alumina support used may be in the form of granules 14/28 mesh or 5/32-inch pellets. The preferred support has a large pore size and a low surface area to facilitate the dissolution of the coating of polymer that is subsequently formed. The active catalyst surface area/weight ratio is 400-600 m^2/g and pore diameter is 65-150 A°, with a sulfate content less than two weight percent.

Catalyst Regeneration:

Catalyst recovered from a polymerization may be regenerated by oxidation with hot air at 540°C in the same way as for the original activation step. Too high an activation temperature (820°C) results in a marked decrease in catalyst activity. This can be attributed to a reduction of the proportion of chromium that is in the hexavalent state. Some poisons are water, oxygen, carbon monoxide, compounds of sulfur, oxygen, nitrogen and halogens. Oxygen at temperatures of 150°C or less acts as poison, apparently through a reversible adsorption.

Steam-aged silica-alumina covered with a 0.8 molar solution of aqueous chromium inoxider is allowed to stand several minutes, and the excess solution is filtered. Impregnated material is dried at 100-200°C and then activated by fluidizing with air at 540°C for 5 hours to give a catalyst containing 2-4 weight percent of chromium.

APPENDIX 3. ADDITIONAL INFORMATION ON EARTHBOUND FLUIDIZED BED POLYMERIZATION

Although the catalyst has a particle size in the range of 40 to 100 mesh, finer (e.g., microspheroidal) particles may be used. The reaction temperature is 200°F to 230°F, which is just below the polymer melting point of 240°F to 260°F. The preferred operating pressure range is 25 to 500 psig. A linear velocity of 0.5 to 1.0 feet/second may be used if dilute phase operation is desired. A particular technique is suggested to prevent agglomeration of catalyst particles by polymer. This involves initial operation of fresh catalysts for 30 minutes to 2 hours at a pressure from 25 to 80 percent of the full process operating pressure. This pre-conditioning step builds up a small amount of polymer which then prevents further agglomeration. This step may be carried out in a first fluidized reactor, delivering the conditioned catalyst to a second polymerization reactor.

APPENDIX 4. CONTROLLED GRAVITY (BASED ON REFERENCE 22).

The validity of the magnetic zero gravity simulation depends on the properties of the magnetic fluid and the characteristics of the field that supplies the magnetic forces.

A suspension was produced by dispersing submicron particles of magnetic iron oxide (Fe_3O_4) in a medium of normal heptane. An extremely stable, low-viscosity, magnetic colloid system containing a 6.83 weight percent particle concentration was prepared in this manner. The particles were essentially spherical in shape, uniformly distributed throughout the liquid, and approximately 0.1 μ in diameter. No significant changes were observed in the boiling point and apparent viscosity. The stability of the colloid system was also unaffected by the earth's gravity or applied magnetic forces in fields of 50 kilogauss, which yield magnetic gradients of 9.1 kilogauss per inch. Under these forces the particles remained dispersed throughout the liquid for extended periods of time.

The apparent stability of the colloid allows an assumption to be made concerning the equivalency between magnetic body forces and gravitational forces. Consider a microscopic volume consisting of a magnetic particle surrounded by a volume of liquid. The influence of the magnetic body force on the system is essentially limited to the solid particle. The particle experiences a force in the direction of the magnetic gradient and, in turn, influences a specific volume of the fluid by some adsorption mechanism, so that magnetic force is transmitted to the liquid. The apparent stability of the system suggests that the applied forces are smaller than the forces that hold the solid liquid systems together, even though calculations showed that the distance between particles is about five times the diameter of the particles themselves.

APPENDIX 5. DESCRIPTION AND MODEL DEVELOPMENT FOR LOW GRAVITY

Force and Displacement in Slurry and Fluidized Beds

Solid phase. Although the basic flow schemes will remain the same, each unit will present new design and operational problems because of the low gravity environment. Under a reduced-gravity condition, the forces required to suspend particles are as follows:

- Drag force on the particle. The gas or fluid stream flowing through the vessel will lose momentum to the particles. The net force on the particle will be parallel to the flow direction of the fluid.
- Particle impact at solid surface. The propeller blade transfers momentum to the particles and the particles in turn lose momentum at the walls.

- Surface tension and Marangani Flow. The surface tension forces between gas and solid are likely to be small relative to drag forces in systems with large circulatory or bulk flows.

- Buoyancy and gravity forces. These decrease to zero as the gravitational field disappears.

No attempt is made to establish mathematically the exact nature of the circulation currents in this study. The injection of gas should be toward the axis of the propeller blade to disperse as many particles as as possible.

Gas phase. Marangani forces on a gas bubble, because of either temperature or concentration gradients and hence surface tension, may influence the bubble motion (23). With pressure pulse, bubbles suspended in a liquid under conditions of weightlessness will approach one another if the natural frequencies of bubble oscillation are greater or smaller than the pulsation frequency, and vice versa. A bubble situated close to the wall of the vessel will move toward the wall during a pressure pulse (24). In non-pulsing flow, bubble formation is encouraged by the forces emanating from the mechanical agitator. In the presence of solid particles, it is difficult to estimate whether bubbles will form and if they do, to what extent they will grow.

Typical earth analysis. The gas velocity required for incipient fluidization (when particles first begin to rotate) has been shown by Davidson and Harrison (25) to be given by

$$U_o = 0.00114\ g\ d^2\ (\rho_s - \rho)/\mu$$

in which:

U_o = superficial velocity of fluidizing medium, cm/sec

g = gravitational acceleration

d, ρ_s = particle diameter and density, respectively

ρ, μ = fluid density and viscosity, respectively

Apparently as gravitational acceleration is reduced, the velocity of fluid necessary for fluidization is also reduced.

A gas bubble in a fluidized bed differs from that in a liquid in that particles and gas enter and leave it. Its rise velocity is given by

$$U_b = 0.71\, g^{1/2}\, V^{1/6} \left[(1-\epsilon_o) / \left(\frac{\rho_s}{\rho_s - \rho_f} - \epsilon_o \right) \right]^{1/2}$$

in which:

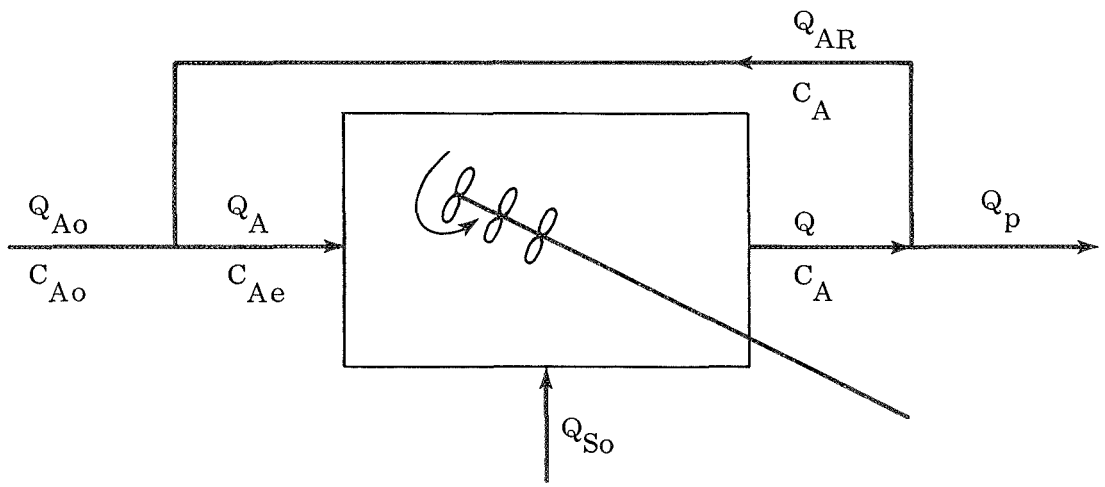
V = volume of the bubble

ϵ_o = void fraction at incipient fluidization

Here again, one would expect bubble velocities to be significantly reduced at low gravity. Whether a bubble will form or not at near zero gravity is in doubt, with only a slight understanding of fluidized bed bubble formation at unit gravity to act as guide. Some non-reactive simulated solid-gas mixing studies will be needed.

Conservation equations

As an example, the conservation equations are derived for a slurry reactor. The method, with some modifications, may be extended to a stirred fluidized bed.



Component balances across reactor. Assuming good mixing, the reactor may be schematically represented as above. The quantities

are defined as follows:

C_A, C_{Ae} = concentration of ethylene leaving reactor, and entering reactor, moles/vol.

C_p = concentration of polymer leaving system

Q = volumetric flow rate, vol/time

Accumulation = Net input + Generation rate

$$\frac{dC_A}{dt} = Q(C_{Ae} - C_A) + R_A V$$

The reaction in terms of ethylene consumption may be depicted as

$$n\ C_2H_4 \longrightarrow (C_2H_4)_n, \quad \text{where} \quad n \approx 1,400$$

with a rate expression for ethylene formation

$$R_A = -R_p = -kC_{xo}\ C_A\ (1 + KC_A)$$

in which: $k = k_o \exp(-E/RT)$, a temperature dependent quantity, and C_{xo} is initial catalyst concentration. The dependence on catalyst concentration was obtained from Friedlander's (26) work on molybdenum/alumina. An alternative rate expression for a Langmuir-Rideal mechanism as shown before is

$$R_A = k\ C_{xo}\ C_A^2 / (1 + KC_A)$$

At steady state, from the recycle node at the entrance

$$Q_A = Q_{AR} + Q_{Ao}$$

and from an overall balance

$$Q_p = Q_{Ao} + Q_{So}$$

The recycle rate may be maintained by controlling the overall residence time which in turn controls the desired conversion. There may very well be an optimum value of recycle rate.

Energy balance

$$\frac{dU'}{dt} = q - P\frac{dV'}{dt} - \Delta\left[W\left(u + PV + \frac{1}{2}\,\frac{\langle v^3 \rangle}{\langle v \rangle}\right)\right]$$

in which U', V' = Internal energy and volume of system, respectively
u, V = Intensive (unit mass basis) for these properties
q = Heat input
v = Velocity of fluid
W = Flow of mass into system = ρQ

At steady state, if kinetic energy is neglected

$$q = -\Delta\left[\rho Q h\right]$$

where h = enthalpy of fluid (mass basis) and h is primarily dependent on the heat of reaction

$$\Delta h_r = -.9 \text{ k cal/g } C_2H_4 \text{ reacted}$$

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